SYNOPSIS

Ph.D in Physics

Surfactant Templated Silica Surfaces as UV, Scratch, and Dust Resistant Antireflective Coating for Improved Solar Cell Performance

Submitted by

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1. Introduction

Energy can be considered as one of the fundamental requirements of life. There has been an increase in energy demand in recent years as a result of population growth and industrial development. Renewable energy resources have the potential to address the energy crisis to an extent because of their large availability and capacity to refill them in less than a human life without diminishing the planet's resources[1]. Among the various renewable energy resources, solar energy is the most promising form of renewable energy and is the most sustainable solution to the energy crisis all over the world. Among them, photovoltaic devices are appraised as the most suitable solar energy harvester. The solar cell needs protection from harsh environmental conditions for better performance and is generally provided by the cover glasses. The performance of a solar cell integrated with a cover glass depends on the amount of radiation within a particular range of the solar spectrum that passes through the cover glass and reaches the photovoltaic semiconductor. A part of the incoming radiation incident on the surface of the cover glass is reflected before reaching the active solar layers. Reflection is usually a detrimental phenomenon that takes place at the interface between the substrate and transmitted media because of the quick change in refractive index from air to the substrate and causes a loss in the efficiency of the solar cell. It is worthwhile to reduce the amount of radiation reflected from the incident glass substrate for reaching maximum solar radiation to the active layer for the enhancement of efficiency[2].

Antireflection coatings (ARCs) are predominantly utilized to suppress the Fresnel reflection losses when light propagates from one medium to another medium. Antireflection coatings for substrate surfaces not only limit unwanted reflection effectively but also improve the performance of optical devices by increasing transmission. The surface of the substrate combined with air on a subwavelength scale such as a porous or textured surface would have AR properties. It is difficult to attain the refractive index of coating of about 1.22 since the low index materials (MgF_2, SiO_2) have a refractive index above 1.38. This problem can be solved by inducing pores into the antireflection coatings[3]. Along with optical transparency, an antireflection coating must guarantee mechanical stability and Self-cleaning ability for the long-term performance of the photovoltaic cell.

Among the various techniques, the sol-gel technique has been chosen to be the simplest and most promising method for the preparation of AR coating due to the ability to tailor the microstructure of the deposited film by inducing porosity. Sol-gel silica film with surfactant texturization improves pore volume, pore distribution, adhesion, and mechanical stability[4]. Several studies have been reported with porous silica material to enhance light transmission, in which most of the researchers used TEOS as the major precursor of SiO_2. **Qianying Zhang** et al., fabricated a single layer SiO_2 coating using TEOS as the major precursor and deposited it on the glass substrate using the dip-coating method. Further, it was modified with dimethyl silicone to enhance its hydrophobic and adhesive properties[5]. **Attila Abraham** and his co-workers prepared TEOS/MTES based durable microporous transparent coating with CTAB surfactant. High transmittance of 99.8% was obtained at 632nm wavelength with a refractive index of 1.25[6]. Most of the researchers only reported the preparation and different characteristics of AR film and did not attempt to demonstrate its applicability in PV solar cells. So the major objective of this work is,

- To select suitable materials for the fabrication of the AR coating without any degradation in material properties under solar radiation.
- Optimization of coating by tuning the concentration of sol and annealing temperature.
- Comparison of transmittance of the coating obtained from UV-Vis spectrophotometer and calculation using solar insolation reading.
- To analyze the self-cleaning performance and stability of the prepared coatings.
- Evaluation of the performance of the coatings on solar cells for the application of solar panel cover glasses.

2. Organization of the Thesis

This thesis comprises of eight chapters as below:

- **Chapter I** provides a brief introduction to renewable energy resources and energy demands. A detailed description of the photovoltaic cell as a solar energy harvester and the need for antireflection coating for the efficiency enhancement of the PV cell.
- **Chapter II** provides a detailed literature review of antireflection coatings (ARC's)
- **Chapter III** provides a detailed description of materials and methods used for the preparation of ARC's.
- **Chapter IV** deals with the different characteristic studies of prepared ARC's (TEOS/PF-127, VTES/PF-127, MTMS/PF-127, MTES/PF-127, and VTMS/PF-127).
- **Chapter V** deals with the mathematical calculation for finding the transmittance of coated substrates using solar insolation reading obtained via Pyranometer and its comparison with UV-Visible transmittance obtained via UV-Visible spectrophotometer.
- **Chapter VI** deals with the characteristic studies of PFOTS modified ARC's.
- **Chapter VII** deals with the performance evaluation of solar cells with prepared ARC's.
- **Chapter VIII** provides the summary of the entire work.

3. Materials and Method

Antireflection coating using five different silanes like Tetraethoxysilane (TEOS), Vinyltriethoxysilane (VTES), Methyltrimethoxysilane (MTMS), Methyltriethoxysilane (MTES), and Vinyltrimethoxysilane (VTMS) along with polymeric surfactant Pluronic F-127 (PF-127) was prepared by acid catalyzed sol-gel method. In the first step, an appropriate amount of Ethanol, Hydrochloric acid and deionized water were mixed in a beaker and stirred for a while. After that, an optimized amount of polymeric porogen Pluronic F-127 (PF-127) was added to the solvent and stirred continuously for 30 minutes at room temperature to get homogeneous polymeric sol. An appropriate amount of silica precursor was drop wisely poured into the polymeric sol and further the magnetic stirring was continued for 2 hours to obtain the transparent Silica/PF-127sol. Finally, the sol was left for aging for about two-three hours at room temperature. During aging, the sol undergoes

hydrolysis and polycondensation at a very slow rate. After that, the sol was used for the deposition of the mechanically stable broadband antireflection coating on glass substrate by spin coating technique at various spinning speed.

The non-wettability to the prepared AR coating was induced by using 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PFOTS) sol. In this stage sufficient amount if PFOTS was dissolved in Hexane using magnetic stirring for 30 minutes and kept at room temperature for 30 minutes. Finally the PFOTS sol was deposited on the coated glass slide using nebulized spray pyrolysis and then annealed at 120°C for an hour in muffle furnace.

4. Sample Characterization

The optical transparency of the coated substrate was measured at room temperature using a UV Visible spectrophotometer (JASCO V-670). The refractive index and thickness of the coating were determined using Ellipsometer (J.A.Woolam Co.) in the wavelength range of 300-900nm. The surface morphology of the coating was analyzed using Field Emission Scanning Electron Microscope, FESEM (ZEISS-Gemini). The porous nature of the sample was determined using Brunauer-Emmet-Teller (BET, Nova Station A). Fourier Transform Infrared Spectroscopic study was carried out using a SHIMADZU spectrophotometer to determine the chemical composition of the sample. The thermal stability of the coating was analyzed using Thermogravimetric analysis (TGA-EXSTAR/6300). The wettable behaviour and surface roughness of the coating was evaluated using the OCA15EC contact angle interface system and surface profiler (Zeta 20) respectively. To evaluate the hardness of the coating, the prepared AR coated substrates were subjected to the Pencil Scratch test, according to the ASTM standard D 3363- 05[7] using different hardness graded pencils (9B-9H). The impact of the pencil scratch on the coating was analyzed using an image analyzer. The stability of the AR coating against UV light was tested by exposing the samples under UV-B irradiation for various time intervals and followed by the transparency analysis. The solar radiation transmittance of the coated substrate was calculated using solar insolation reading from Pyranometer using ASTM E 1918-97[8]. The reading was taken for the different time periods on a sunny day (March, April). These readings were further used for calculation. The photovoltaic performance of the AR coating as a cover glass of a

photovoltaic module was evaluated by using commercially available polycrystalline silicon solar cell under simulated 1000W/m^2 illumination (AM 1.5G) in air.

5. Results and Discussion

5.1 Fourier Transform Infrared Spectra (FTIR)

The molecular vibration contained in the prepared sample was determined by FTIR analysis at room temperature within the wave number range 400-4000 cm^{-1}. Regarding the fingerprint (500-1500cm^{-1}) region strong band appeared at 594cm^{-1}, 1074cm^{-1}, 1025cm^{-1} and 1082cm^{-1} indicates asymmetric stretching vibration of Si-O-Si group, whereas the band that appeared at 1018cm^{-1}, 1091cm^{-1},957cm^{-1} indicates the stretching of Si-O-C group[9], [10]. The characteristic band appeared in the wave number range 1600-1690cm^{-1} indicates C=C stretching vibration which attributes to the presence of the vinyl group in the sample. A small peak observed at 2885 cm-1 indicates the C-H aliphatic stretch of PF-127. The band appeared at 1150, 1246, 1389, and 1519 cm^{-1} associated with both PPO and PEO parts of PF-127[11]. Besides, the band at 3484 cm^{-1} and 3649 cm^{-1} were responsible for the stretching vibration of –OH in PF-127.

5.2 Optical Properties using UV-Visible Transmittance spectra

5.2.1 Effect of PF-127 on AR property of coating

The optical performance of the prepared antireflection coating was analyzed by UV-Visible transmittance spectra within the visible region of 400nm-800nm. The concentration of Pluronic F-127 in the sol was optimized for the best transmittance value and was deposited on a cleaned glass substrate by spin coating with different spinning speed for one minute and followed by annealing at 120ºC for an hour to remove the solvent from the film. The transmittance of the uncoated glass substrate was compared with pristine silane coating and Silane/PF-127 coated glass substrate. An improvement in the transmittance of Silane/PF-127 compared to bare glass and pristine coated glass confirms the influence of the polymeric surfactant in the silica network of the hybrid film.

5.2.2 Effect of Annealing Temperature

To understand the influence of annealing temperature on the optical performance, the optimized sol deposited glass substrate was heat-treated at various temperatures (100-350°C) for an hour and then analyzed its transmittance spectra. From the spectra analysis, it is clear that the transmittance of the coating increases with increasing annealing temperature up to an optimized temperature. The improvement in the optical transmittance during heat treatment implies a reduction in refractive index and film thickness and was confirmed by Ellipsometric analysis. The reduction in the refractive index of the coating indicates an increased porosity due to the decomposition of the surfactant. The decrease in the transmittance of coating heat treated above an optimized temperature indicates the increase of scattering due to the enlargement of pore size, which was further confirmed by BET analysis.

The transmittance of the sample modified with PFOTS was also analyzed using a UV-Visible spectrophotometer and a small variation in transmittance was observed as compared to unmodified samples.

5.2.3 Transmittance calculation using Solar Insolation reading

Mathematical relations were used to calculate the transmittance of the Silane/PF-127 based AR film when a solar beam of radiation was incident on the exterior of the glass surface at various incident angles. Transmittances of the coated glass for different incident angles have been computed. From **Duffie and Beckman**, the unpolarized solar radiation can be divided into parallel and perpendicular components (r_{II} and $r_{\perp}$), which can be determined using the relation[12],

$$r_{\perp} = \frac{\sin^2(\theta_r - \theta_i)}{\sin^2(\theta_r + \theta_i)} \qquad (1)$$

$$r_{II} = \frac{\tan^2(\theta_r - \theta_i)}{\tan^2(\theta_r + \theta_i)} \qquad (2)$$

The reflection of the unpolarized radiation can be calculated as the average of the two components,

$$\rho = \frac{1}{2}(r_{\perp} + r_{II}) \quad (3)$$

For the normal incidence of solar radiation both the θi and θr are zero, then the equation (2) become,

$$\rho = \left(\frac{n_{air} - n_{glass}}{n_{air} + n_{glass}}\right)^2 \quad (4)$$

In the calculation of transmittance of unpolarized radiation through the AR glass, both absorption and reflection loss should be taken into consideration. By considering transmittance, the reflectance loss was determined by,

$$\tau_{reflect} = \frac{1}{2}\left(\frac{1-r_{II}}{1+r_{II}} + \frac{1-r_{\perp}}{1+r_{\perp}}\right) \quad (5)$$

Absorbance loss by considering transmittance,

$$\tau_{absorbance} = \exp\left(-\frac{k\delta_c}{\cos\theta_r}\right) = \frac{I_L}{I_{bn}} \quad (6)$$

(Where, δc − is the thickness of the glass, k- extinction coefficient of glass, IL-Radiation flux after passing through glass and, Ibn –Radiation flux before passing through the glass.) Calculated transmittance of the AR glass was determined by the equation,

$$\tau_{out} = \tau_{absorp}\, \tau_{reflect} \quad (7)$$

The obtained angle of incidence (θi), angle of refraction (θr) and corresponding transmittance for bare glass and, coated glass were calculated.

The result obtained infers that the calculated transmittance values of AR coating show good agreement with UV-Vis transmittance values.

5.3 Morphological & Elemental Analysis

The morphological evolution of the Silane/PF-127 based samples heat-treated at different temperatures and PFOTS modified coatings were recorded using Field Emission Scanning Electron Microscopy (FESEM). The Silane/PF-127 based coating heat treated at 100°C showed smooth, uniform and crack-free surface, where as coating heat treated at 250°C,

300°C and 350°C showed porous structure morphology indicated the effect of annealing. Also the morphology showed an enlargement in pore size during heating. The changes in the elemental composition during annealing were recorded using EDAX measurement. The result obtained for the samples annealed at 100ºC, 250ºC, 300°C and 350°C are compared. The sample annealed at 100ºC shows the presence of Si, O, and C as the major constituent of Silane/PF-127. But in the case of the sample annealed at 250ºC and 300°C, the occurrence of O and Si at the surface of the specimen in extensive quantities was found but a decrement in the percentage of C atom. The reduced weight percentage of C atom indicates the decomposition of Pluronic F-127 and the major phase of SiO_2, since PF-127 begins to decompose in the temperature range 220°C-500°C[13]. The EDAX analysis of the samples modified with PFOTS reveals the elemental presence of F and Cl in the sample.

5.4 BET Analysis

To analyze the porous structure of the Silane/PF-127 coating, nitrogen adsorption-desorption analysis is required, which includes pore size, pore volume, and surface area test. The N2 adsorption-desorption isotherms and pore size distribution of the sample prepared at various temperatures were analyzed. As per the IUPAC classification, the N2 adsorption-desorption isotherms of all samples annealed at 100°C, 250°C, and 300°C exhibit Type IV isotherm, indicating the presence of mesopores (3nm-50nm). The BET analysis reveals the enhancement of pore size during annealing validates the scattering of light above an optimized temperature due to large pore size.

5.5 Thermal Analysis

The porous structure of the Silane/PF-127 based film is related to the decomposition of the polymeric surfactant PF-127 during heat treatment. The thermal stability of the prepared coatings was analyzed using TGA analysis. The weight loss of the samples during different stages was identified. Among the five different sets of samples MTMS/PF-127 sample showed multistage decomposition. The weight loss observed in the first stage indicates the decomposition of both the PF-127 and methyl group of MTMS, where as second stage decomposition indicates the decomposition of Si-C of MTMS[14]. All the five sets of samples show good thermal stability.

5.6 Stability of the Silane/PF-127 based coating

5.6.1 Mechanical stability of the coating using pencil scratch test

Scratch resistance of the prepared single-layer AR coating against different pencils (9B-9H) was investigated according to the ASTM standard D3363-05 method. Here in this method, the pencil was firmly held against the coated substrate placed on a horizontal surface at an angle of 45º and moved over the sample. Changes in the surface of the prepared samples were analyzed using an image analyzer. The TEOS/PF-127, VTES/PF-127, MTMS/PF-127, MTES/PF-127 and VTMS/PF-127 coatings showed good scratch resistance against H, 9H, 4H, 3H and 7H hardness pencils respectively.

5.6.2 Environmental Stability of coating under UV-light irradiation

The environmental stability of the coating against UV light was determined by exposing the Silane/PF-127 sample under a UV-B light source of 50W. The distance between the light and the sample was kept at approximately 10cm to avoid the thermal heating of the sample due to the radiation. The % transmittance change of the coating after UV light exposure for 50 hours was recorded. The TEOS/PF-127, VTES/PF-127, MTMS/PF-127, MTES/PF-127, and VTMS/PF-127 coatings showed good stability under UV-light exposure.

5.7 Surface Roughness and Contact Angle

Surface roughness plays a major role in the wettable behaviour of the coating. The roughness of the samples TEOS/PF-127, VTES/PF-127, MTMS/PF-127, MTES/PF-127 and VTMS/PF-127 were analyzed using 3D laser profilometry and showed a roughness of 0.45μm, 0.6μm, 20.1μm, 21.6μm and 1.37μm with water contact angle 9°,21°, 98°,103°, and 62° respectively. After the modification using PFOTS sol, the coatings except TEOS/PF-127/PFOTS showed an improvement in roughness and water contact angle with the hydrophobic properties.

5.8 Solar cell Performance Evaluation

To assess the practicality of the multifunctional Silane/PF-127 based single layer AR coating on the cover glass for solar panel, the coated specimen was placed over the commercially available polycrystalline solar cell (Loom Solar) and its photovoltaic performance was measured. The I-V characteristics of the solar cell were performed under five different conditions ‘with bare glass, with coated glass, with PFOTS modified coated glass, PFOTS modified glass with dust, PFOTS modified glass after cleaning. The solar cell with all the TEOS/PF-127, VTES/PF-127, MTMS/PF-127, MTES/PF-127, and VTMS/PF-127 coatings showed an enhancement in efficiency than the bare glass. The coatings modified with PFOTS except TEOS/PF-127/PFOTS showed better efficiency as well as self-cleaning performance. The improvement in the total conversion efficiency of the solar cell validates the light-trapping ability of the prepared Silane/PF-127 based porous structure and can be considered a promising antireflecting cover glass for photovoltaic systems.

6. Conclusion

- Silane/PF-127(TEOS/PF-127, VTES/PF-127, MTMS/PF-127, MTES/PF-127, and VTMS/PF-127) based multifunctional antireflection coatings are deposited on the glass substrate successfully and were characterized by FTIR, UV-Visible, FESEM, EDAX, BET, TGA, Surface roughness analysis, Contact angle, Pencil scratch test, UV-Irradiance, and I-V characterization.
- All the prepared coating showed an improvement in the optical transparency as compared to the bare glass.
- The wetting property of the prepared samples was enhanced by depositing PFOTS using spray coating.
- The potentiality of the prepared coatings for solar cell cover glass was analyzed using I-V characterization under different conditions and the coatings showed enhancement in efficiency as compared to the bare glass.
- The solar cell along with coated cover glasses retains its efficiency even after exposure to dust due to good self-cleaning ability.

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Publications

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